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Mathematical modeling of glow peaks of fluorites relevant to dosimetry and dating

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Abstract : Mathematical modeling of glow peaks (as many as eleven in the range of 30-600°C) of fluorites (light green) of Indian origin relevant to dosimetry and dating, has been successfully achieved to a high degree of certainty in the frame work of general order kinetics formalism. The criteria to accept the goodness of fit between the experimental glow curve and the numerically generated best fit curve, is judged not from the figure of merit (FOM) as conventionally done but from a rather rigorous criteria *i.e.* the Chi-square (χ^2) test. With this achievement, it has been possible to estimate the lower limit lifetime (τ) of electrons trapped at deep levels of fluorite. The values of τ is found to lie in the range of 10^{16} - 10^{21} years at 300°K. Thus, the high temperature glow peaks have potential use in determining the time of mineralisation of the material. In fluorite, these glow peaks occur at 398°C, 439°C, 477°C and 545°C for a moderate heating rate (β) of 0.25°Cs^{-1}

Keywords Thermoluminescence, mineralisation, glow curve deconvolution, lifetime

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1. Introduction

Thermoluminescence (TL) of minerals has been observed for many centuries. However as far as fluorite is concerned, the earliest detailed works appear to be that of Iwase as early as 1933 [1,2]. Subsequently, Daniel and Saunders [3] while studying TL of fluorites, noted that TL response in fluorites varied according to the colours. In the last 50 years, a considerable volume of literature has accumulated not only on TL of fluorites but also on CaF_2 based TLDs, references to which can be found in the reviews [4,5] and books [6,7]. Fluorite is well known for its high TL sensitivity; the light green transparent variety being the one having the highest TL sensitivity [8]. The materials both in natural and synthetic-forms doped with suitable activators have been extensively studied for possible applications in radiation dosimetry and geology [9 -13].

Fluorite is known to have prominent glow peaks around 75°C, 150°C and 225 - 250°C with additional weaker peaks around 350°C, 450°C and 500°C [5]. The highest temperature at which glow peak can be obtained in fluorite is at about 650°C for a heating rate of 17°Cs^{-1} [14]. This is believed to be associated with Sm impurity coexisting with Y, La or Ce in CaF_2. A number of workers have attempted to analyse the glow curves of fluorite, reference to which can be found in the book of McKeever *et al* [7]. The values of the trapping parameters as determined by Computerised Glow Curve Deconvolution (CGCD) by Ganguly and Kaul [15] are more or less accepted by the TL community in the sense that this Indian work has been well documented in the standard text on TL [7,16]. It is to be noted that Ganguli and Kaul's work is confined to the zone of 20 to 500°C.

In this paper, we demonstrate that the high temperature glow peaks of fluorites can be easily recorded once the sample is heated with a rather relatively slow heating rate ($1 \geq \beta \geq 0.25$°C s^{-1}). This procedure allows shifting of the glow peak temperature to the region less obstructed by the black body radiation. Further, an uncontaminated glow curve gives better data for subjecting to rigorous CGCD which helps in better estimation of the life time (τ) of the electron trapped. The prediction of lifetime of a TL peak of a datable material is useful in establishing the likely time span over which it will be useful for dating. Larger the lifetime, more is the upper limit of dating. Materials having

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TL peaks, whose lifetime is more than a billion of years, are potential candidates to predict the possible time of mineralisation.

2. Experimental

Glow curves of fluorites of light green variety of Indian origin (obtained from M/S The Hindustan Minerals Natural History Specimen Supply Co., Calcutta) is recorded with the help of Risø (Denmark) TL/OSL reader (model TL/OSL-DA-15). The equipment is an upgraded TL/OSL reader [17, 18]. It has been used worldwide for TL/OSL dating, retrospective dosimetry, environmental dosimetry and material characterisation.

All the glow curves are recorded with various heating rate in nitrogen atmosphere. The photomultiplier tube used is EMI 9635. The operating voltage is 950 volts. Optical filter Schott UG-11 in conjunction with Schott BG-39 is used in filtering out the unwanted radiations. This combination allows transmission in the wavelength range of ~ 300 to 400 nm.

In each experiment, 5mg of powdered fluorite is heated from room temperature (20°C) to 575°C. The rate of heating is varied from 0.25°Cs^{-1} to 5°Cs^{-1} depending upon the need.

A second readout is performed to record the background radiation which includes the background radiation. The data presented are all with the background subtraction.

3. Result and discussion

Glow curves of light green fluorite irradiated with 1Gy dose of beta recorded with various rates of heating namely, 0.5°Cs^{-1}, 1°Cs^{-1}, 2°Cs^{-1}, 5°Cs^{-1} are shown in Figure 1.

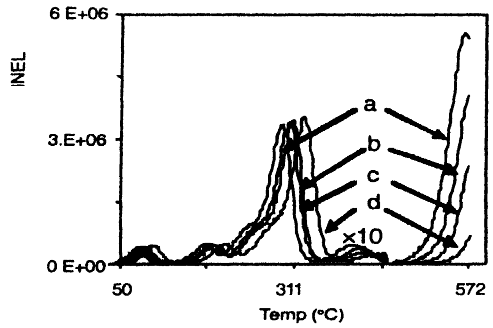

Figure 1. Glow curves of natural fluorites (light green) irradiated with 1Gray of β-radiation with various heating rates. (a) 0.5°Cs^{-1}, (b) 1°Cs^{-1}, (c)2°Cs^{-1}, (d)5°Cs^{-1}.

In general, for dating and dosimetry purpose one use a heating rate of 5°Cs^{-1} or more. In the present case, heating rates lower than 5°Cs^{-1} have been resorted because even with the careful subtraction of the background radiation of the signal in the region of 500°C to 575°C, significant TL is observed. For a heating rate as low as 0.5°Cs^{-1}, the glow curves clearly reveals the presence of rather intense peak at 566°C (Figure 1). This is not unexpected if one keeps in mind the presence of a glow peak at about 650°C in fluorite for heating rate of 17°Cs^{-1} [14]. Other than this high temperature glow peak, for β = 0.5°Cs^{-1}, the glow curve shows peaks at 76°C, 182°C, 236°C, 496°C and 400°C. In order to locate the hidden peaks, fourth derivative plots of the glow peaks have been plotted. One such plot is shown in Figure 2.

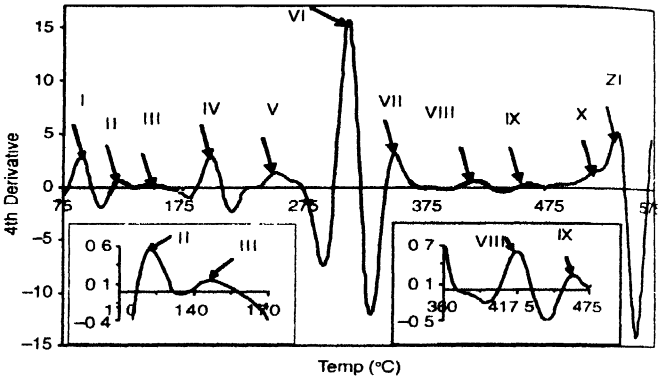

Figure 2. Fourth derivative plots of the glow curves of fluorite (light green) irradiated with 1Gray of beta radiation with heating rate = 2°Cs^{-1} (The temperature range 110 - 170°C and 360 475 °C which are represented by thicker line in the graph are shown in expanded form in the inset).

The plot shows the presence of weak peaks (located by the maximas). The glow peak temperatures as obtained from the maximas of the fourth derivative plots, are presented in Table 1

Table 1. Glow peaks of fluorite and their trapping parameters (E and s) (T_m's are located from the 4th derivative of the glow curve).

Heating rate (°Cs^{-1}) →	0.5	1	2	5	VHR	
Peak No. ↓	Peak temperature in (°C)				Energy (eV)	Frequency factor (s^{-1})
I	78	86	90	104	0 96	2.8×10^{12}
II	114	120	128	140	1.07	5.7×10^{12}
III	132	140	150	164	1.02	2.1×10^{11}
IV	184	192	198	214	1 39	1.0×10^{14}
V	236	246	254	268	1.56	1.0×10^{11}
VI	296	308	312	330	1.93	5.0×10^{15}
VII	342	352	360	372	2.38	1.1×10^{15}
VIII	400	412	418	436	2.56	4.8×10^{18}
IX	450	462	466	490	2.54	1.0×10^{15}
X	504	520	538	548	2.6	1.3×10^{15}
XI	566	-	-	-	-	-

Having obtained the peak temperatures of the glow peaks under various heating rates, the corresponding trap parameters, namely, the activation energy (E) and frequency factor (s) have been determined using the following well known equations of Hoogenstraaten [19] according to which

$$\ln\left(\frac{\beta}{T_m^2}\right)=\ln\left(\frac{SK}{E}\right) \qquad KT_m \tag{1}$$

Eq. (1) is strictly true for glow peaks following first order kinetics. However, critical appraisal of the use of the method have shown that it yields a very good approximation of E for practically any kinetic order [20] and even if the frequency factor is temperature-dependent [21]. The values of E and s thus obtained, are presented in Table 1.

The high temperature glow peaks observed by El Kolaly *et al* [14] at 650°C for a heating rate of 17°Cs^{-1}, have been advocated to be candidates for UV dosimetry (by phototransfer) and geological dating *i.e.* age of mineralisation. Keeping these two points in mind the high temperature peaks are separated from the lower ones by suitable thermal cleaning. A set of such glow curves are shown in Figure 3. The heating rates used are low so

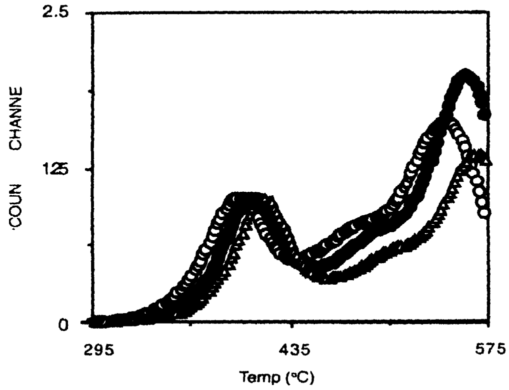

Figure 3. Glow curves of natural fluorite (*i.e.* NTL) preheated to 450°C with various heating rates ooooooo 0.25°Cs^{-1}, ●●●●●● 0.50°Cs^{-1}, ΔΔΔΔΔΔΔ 0.75°Cs^{-1}.

as to locate the high temperature glow peak. These glow peaks are subjected to Computerised Glow Curve Deconvolution (CGCD) in the frame work of the general order kinetic. The following general order kinetic [22] equation in conjunction with the condition for maxima is used for CGCD.

$$I(t)=n_0 s\exp\left(-\frac{E}{KT}\right)\left[1+\frac{s(b-1)}{\beta}\int_{T_0}^{T_m}\exp\left(-\frac{E}{KT'}\right)dT'\right]^{-\frac{b}{b-1}} \tag{2}$$

$$1+(b-1)\left(\frac{S}{\beta}\right)\int_{T_0}^{T_m}\exp\left(-\frac{E}{KT'}\right)dT'=\frac{bsKT_m^2}{E\beta}\exp \qquad KT_m \tag{3}$$

The program used for CGCD is similar to the one presented in the book of Chen and Kirsh [20] with the modification that it searches the best value of peak temperature within ± 2°C of the given experimental value.

The results of CGCD are shown in Figures 4 – 6, while output of the fitting *i.e.* the trapping parameters of the best fit glow

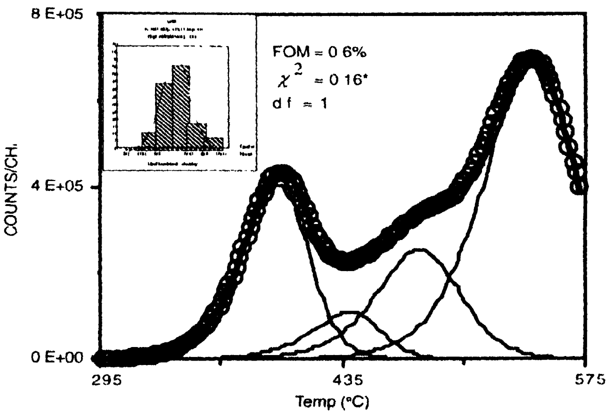

Figure 4. Computerised glow curve deconvolution of natural fluorites (heating rate = 0.25°C s^{-1}). oooooo Experimental glow curve, ——— Fitted curves, ——— Sum of the fitted curves [Inset shows histogram of error, figure of merit (FOM), degrees of freedom (d f), Chi square (χ^{2**}) and ** accepted at 5% level of probability (LOP)]

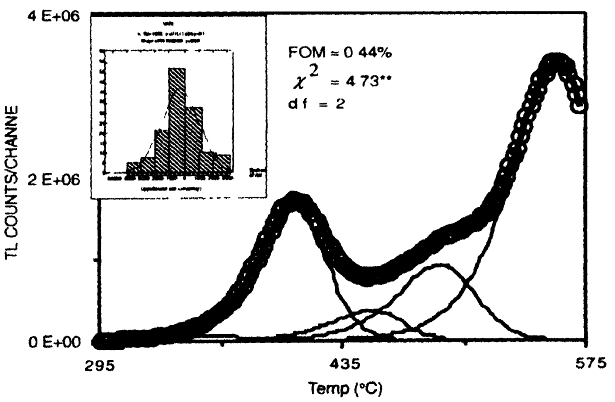

Figure 5. Computerised glow curve deconvolution of natural fluorites (heating rate = 0.5°Cs^{-1}) oooooo Experimental glow curve,—fitted curves, ——— Sum of the fitted curves. [Inset shows histogram of error, figure of merit (FOM), degrees of freedom (d f.), Chi-square (χ^2 **) and ** accepted at 5% level of probability (LOP)].

peak are presented in Table 2. The values obtained by VHR are also presented in the same table for comparison. The agreement between the values given in the two tables is very good. This justifies the utility of VHR [20, 21]. Further, this also supports the utility of CGCD which has helped in showing that the high temperature glow peaks of fluorite follow non-first order kinetics

Table 2. Trapping parameters of the best fit high temperature glow peak as obtained by CGCD as well as VHR.

Peak No.→		VII	VIII	XI	X	XII
Heating rate (°C/s)	T_m(°C)	338	398	439	477	545
0.25	E (eV)	1.52	2.40	2.48	2.50	2.65
	s (s^{-1})	4.4×10^{10}	4.9×10^{15}	6.8×10^{15}	6.7×10^{14}	3.5×10^{14}
	b	1.01	1.40	1.25	1.50	1.46
0.50	T_m(°C)	362	408	451	491	559
	E (eV)	1.60	2.40	2.50	2.53	2.75
	s (s^{-1})	2.6×10^{9}	1.7×10^{16}	6.7×10^{15}	1.2×10^{15}	1.0×10^{15}
	b	1.01	1.35	1.20	1.30	1.20
0.75	T_m(°C)	368	416	460	499	566
	E (eV)	1.61	2.44	2.48	2.52	2.65
	s (s^{-1})	2.1×10^{11}	3.2×10^{16}	5.2×10^{15}	1.0×10^{15}	2.6×10^{14}
	b	1.09	1.34	1.20	1.20	1.40
VHR	E (eV)	1.35	2.41	2.45	2.55	2.78
	s (s^{-1})	1.5×10^{9}	4.7×10^{16}	5.6×10^{15}	4.2×10^{15}	2.9×10^{15}
	τ (Yrs) at (300K)	3×10^{9}	4×10^{16}	4×10^{18}	1×10^{20}	3×10^{22}

[+] E is the energy, s is the frequency factor, b is the order of kinetics and τ is the lifetime

(b ≠1). The values of figure of merit (FOM) of the fitting show that the peaks are acceptable. In order to further substantiate the value of the trapping parameters obtained by CGCD, we have used the Chi-square (χ^2) test for normality. The histograms of error along with the expected normality are shown in the inset of Figures 4 - 6.

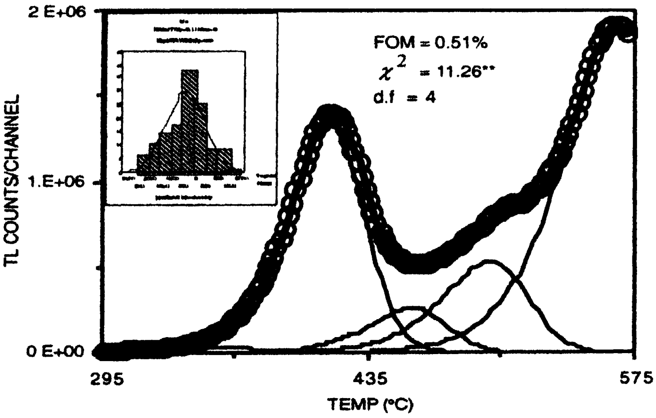

Figure 6. Computerised glow curve deconvolution of natural fluorites (heating rate = 0.75°C /s^{-1}). oooooo Experimental glow curve, ——— Fitted curves, —— Sum of the fitted curves. [Inset shows histogram of error, figure of merit (FOM), degrees of freedom (d.f.), Chi square (χ^{2*}) and * accepted at 1% level of probability (LOP)].

The χ^2 test is one of the most common tests for qualitative measures of significance of departure of experimental results from theory. Test for goodness of normality is given by

$$\chi^2 = \frac{\sum_{i=1}^{k}\{O(I_i)' - I_i'\}^2}{I_i'} \tag{4}$$

where k is the effective number of classes, $O(I_i)'$ is the observed frequency and I_i' is the expected frequency of error distribution (*i.e.* between observed intensity of the experimental glow curve and numerically generated intensity of the glow curve.)

Murti *et al* [23] introduced this χ^2–test in TL glow curve fitting to check randomness of error. If the error is random, it follows normal distribution and then the value of χ^2 is insignificant at least up to the minimum probability level of 1%, which is the lowest critical limit usually assigned to χ^2 distribution for acceptability of the hypothesis; otherwise, 5% level of probability is conventionally taken as the critical limit for the acceptability of the hypothesis [24, 25]. If the hypothesis of normality of error distribution is accepted, then error distribution is random enough and theoretical fitting to the experimental glow curve is the best at that level of probability

The birth of the planet earth itself is about 5×10^9 years The life time of the electron trapped in deep traps of fluorite being 10^{16}-10^{23} years at 300K (Table 2) provides a new avenue of dating the time of mineralisation. The use of TL in dating the age of mineralisation has already been attempted earlier [9, 26-29]. The 650°C high temperature glow peak reported by El- Kolaly *et al* [14] corresponds to the 545°C (for β = 0.25°Cs^{-1}) of present work, since extrapolation of $\ln(T_m^2/\beta) \sim (1/T_m)$ graph using the present result (Figure 3) shows that the peak would occur at 630°C for β = 17°Cs^{-1}.The theoretically generated glow curve for β= 17°Cs^{-1} is shown in Figure 7 having a full width at half

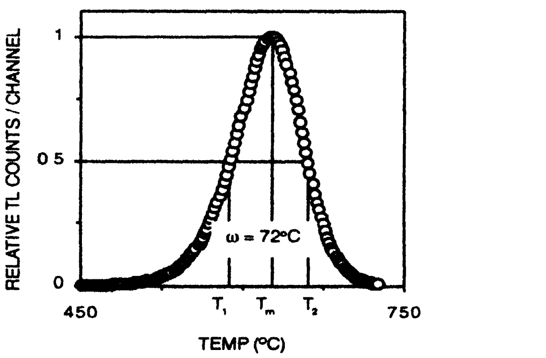

Figure 7. Numerically generated high temperature glow peak for heating rate = 17°Cs^{-1}(input parameters E = 2.65eV, b = 1.4). The full width at half maximum is 72°C.

intensity of ω = 72°C. This agrees with the experimental value of ω obtained by E-Kolaly *et al* [14].

Since the minerals are expected to be buried at a higher temperature than at room temperature (~300K), the life time of peaks relevant to dating is calculated for high temperature (Table 3). This shows that even at 150°C, it is more than billion of years. Thus, it is inferred that the TL peak of fluorite (E = 2.4eV, $S = 5\times10^{15}$) has a rather high unique value of τ which may be exploited for geological dating.

Table 3. Expected life time of electron in traps in peaks VIII and XI relevant to dating the age of fluorites.

Peak temp (°C)	Life time for burial temperature in (Years)					
	20°C	50°C	100°C	150°C	175°C	200°C
398	1.7×10^{20}	2.5×10^{16}	2.4×10^{11}	3.5×10^{7}	1.8×10^{6}	3.3×10^{4}
545	1.0×10^{24}	6.1×10^{19}	1.7×10^{14}	1.0×10^{10}	1.9×10^{7}	4.7×10^{6}

Further, since natural thermoluminescence has been recognized as an investigative tool in the elucidation of temperature of crystallization of a mineral [30], the deep traps of fluorite (in particular the 2.7eV trap responsible for XI peak) have high potential in palaeothermometry.

4. Summary

The lifetime (τ) over which a charge is retained at a trapping level is of fundamental importance in the use of TL as a technique in dating and dosimetry. τ depends on the trapping parameter, activation energy (E), frequency factor (s) and order of kinetic (b) Thus, determination of spectroscopy of traps of materials which include TLDs and geological material, is of practical importance.

In this paper, we report a simple and fast method for the determination of spectroscopy of CaF_2, a system well known for its application in dosimetry. This is achieved by using statistical criteria to judge the goodness of fit between the experimental and the numerically generated best fit glow curve. The large values of the deep traps of fluorite show that charge trapped in these, may find use in the determination of the age of mineralisation.

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